

RETANNING CHROME-TANNED LEATHER*

Wallace Windus

Eastern Regional Research Laboratory
Philadelphia

Introduction

To achieve maximum efficiency and economy, it is customary to tan light leather with chrome by one procedure for the entire production. Splitting and sorting can then be carried out easily and accurately. Retanning permits great flexibility and enables the tanner to "tailor-make" the wide variety of leathers demanded by the market place.

Vegetable tannins, the extracts of bark, wood and pods, are still the most widely used retanning agents by a substantial margin. Chrome retanning is frequently used to raise the hydrothermal stability and increase the mellowness of the leather. Among the older tanning agents, alum and formaldehyde are seldom used for retanning. From a historical standpoint, syntans were the next retanning or modifying agents to become available and continue to be used in large volume. Since the early thirties a remarkable number of tanning and retanning agents have been discovered. They include one effective mineral tan; namely, basic zirconium sulfate. An unusual development has been the proliferation of resin or polymeric tanning and/or impregnating agents. The first was the sodium salt of a styrene-maleic anhydride copolymer. This was followed by methylolmelamine, urea-formaldehyde and dicyandiamide-formaldehyde monomers or polymers. Phenolic tanning agents have come of age and are now adequate by themselves. Glutaraldehyde is a far more effective tanning agent than formaldehyde. The most recent retanning agent is a methacrylic acid copolymer.

The subject of this review is the use of synthetic tanning agents for

retanning chrome-tanned leather with emphasis on glutaraldehyde. The numerous synthetic compounds will be discussed briefly, followed by a longer description of the practical application of glutaraldehyde in the United States. Emphasis will also be placed on side leather since this is the largest branch of the industry using basic chromium sulfate for tanning. It also uses the largest amount of retanning agents. From a chemical standpoint, the discussion also applies to calf, sheep and kid leathers. The industry has so many combinations and permutations that it is impossible to do justice to all leathers.

Inorganic Retanning Agents

One can consider both basic chromium sulfate and basic zirconium sulfate as synthetic tanning agents since they do not occur in nature and must be prepared from their respective ores. Chrome is used as a retanning agent on some lines of leathers. A higher temperature and pH and a shorter time can be used since the hide or skin is already protected by the initial chrome tannage. The shrink temperature, mellowness, water resistance, roundness and perspiration resistance are increased. Retanning with chrome is decreasing in the United States because of the trend to firmer and thicker leathers.

It is less commonly known that zirconium is a useful retanning agent and is widely used for this purpose in the United States. A small amount, on the order of 3-5% of the commercial basic zirconium sulfate based on the blue weight of the leather, tightens and plumps the grain. This improves the break and makes buffing easier. For moccasin and boot leathers, it is usually followed by vegetable retanning.

Syntans

Naphthalene syntans can hardly be considered good tanning agents. However, they continue to be the preferred syntans for bleaching chrome-tanned leather in the production of utility white leather. Phenolic syntans are good tanning agents when they have the proper structure. Those with sulfone bridges also have light resistance. There seems to be some regional variation in their popularity on side leather in the United States. They appear to be used more frequently on side leather in the New England area than in the Midwest. They have some bleaching and filling action as well as influencing the distribution of the oils, the levelness of the dyes and the feel of the grain. These generalities apply to calf, goat and sheepskin leathers on which syntans are frequently used as well as to cowhide leathers.

Polymeric Retanning Agents

A maleic anhydride-styrene copolymer was the first resin tanning or impregnating agent and represented a significant departure and achievement. As a sodium salt, it was widely used for the production of white leather when white suede and crushed grain leathers were in style. It was drummed into depickled skins and acidified to precipitate the carboxylic acid form of the resin. It may tan to the extent of forming hydrogen bonds since the shrink test is raised moderately. It is insolubilized by forming a salt of a mineral tanning agent. Aside from including it for historical reasons, it is in use now by at least one tanner for retanning or impregnating chrome-tanned leather without subsequent fixation. It does have some filling action.

Methylomelamine was the first organic tanning compound capable of producing leather that did not shrink in boiling water. The leather is white and lightfast. The methylol-melamine polymerizes in situ and forms so many cross links by a Mannich-type reaction that the leather is weak when the shrink test is very high. For this reason, together with its cost, a smaller percent is used for retanning chrome-tanned leather in the production of some white leather.

Dicyandiamide-formaldehyde and urea-formaldehyde resins are useful for filling flanks and shoulders. They form hydrogen bonds with collagen. Some are referred to as impregnating agents.

Recently a methacrylic acid copolymer has been introduced for retanning. It has a filling and plumping action. Applications have already been found on splits and sides. It is drummed into the chrome-tanned leather at a moderately elevated temperature. It combines with the leather and does not require any acidification or insolubilization with inorganic salts.

Miscellaneous

Aliphatic sulfonyl chlorides have apparently not succeeded as tanning agents, although they do react with the epsilon-amino group of the lysine residues in collagen to form an amide link and are fixed. They are mono-sulfonyl chlorides and do not cross-link. However, they are used to lubricate washable glove leather.

Glutaraldehyde

Retanning with glutaraldehyde will be reviewed from the standpoint of practical applications on leather that is in regular production. Most uses are based upon procedures and recommendations originating in our laboratory. However, adjustments have been made by tanners to adapt the tannage to their leathers. Tanners have been frank in discussing details and generous in permitting their use. Leathers that I will discuss are available for inspection. They are identified by trade-name and the name of the manufacturer, with the permission of each tanner.

Retanning chrome-tanned leather is usually done in a drum at a temper-

ature of 120° to 140°F. (49-60°C.) for 1 to 3 hours. The amount used varies from 3% to 10% of the commercial 25% solution. Approximately 60% to 70% of the glutaraldehyde reacts in 2 hours. When the leather is retanned with chrome, the aldehyde can be added with the chrome liquor. When the leather is retanned with extracts, it is customary to add the aldehyde first and run the drum for about 30 minutes before adding the extract to the same liquor.

Glutaraldehyde increases the resistance or stability of leather to perspiration and to alkaline solutions. It also improves its washability. These properties have led to the large-scale use of this tanning agent. It is now established as a successful commercial development.

Every tannage has limitations. An awareness of the limitations of the glutaraldehyde tannage will pinpoint potential applications for a new user more quickly and accurately. In view of the diversity of the leather industry, it is understood that a disadvantage on one leather may be an advantage on another. Some of these apparent inconsistencies will appear in the discussion of specific applications. Since the tannage is a commercial success, the limitations have obviously been circumvented or minimized.

Leather tanned with glutaraldehyde alone has a yellow or light tan color. The color of chrome leather is altered in the same direction. This causes complications in the production of white leather and may require a change in the dye formulas for colored leather. A glutaraldehyde retannage increases the mellowness of leather. This is desirable on "softy" leather but is not indicated for moccasin leather. The leather may have a poorer "break," and the grain is too soft to glaze. An organic tannage always seems to wet more readily than a mineral tannage. This is usually considered a disadvantage except when using impregnating finishes. Another disadvantage is less clear-cut and may be the result of a combination of factors. Nevertheless, it seems desirable to mention that there is a fairly general impression that glutaraldehyde retanning lowers the strength of leather. This is not

serious or even very obvious on leather as thick as shoe upper leather, but it does require attention on leather as thin as glove leather.

The improvement in the resistance to perspiration and alkaline solutions conferred by a glutaraldehyde retannage led to the first large-scale application of this aldehyde to work shoe leather. Practical wear tests by employees in a dairy, a paper mill and a gasoline station, where workmen are doing physical labor and where alkaline solutions are used for cleaning, amply demonstrated the longer wear of chrome-glutaraldehyde-tanned upper leather. The new tannage permitted the tanner to drop the manufacture of a chrome-tanned-vegetable-retanned stuffed leather which was more expensive to manufacture. The leather was too mellow initially. This was corrected by modifying the composition of the fat liquor as well as reducing the amount used. This tanner was the first to point out to us that his colors were more level and uniform, which he called a "bonus" property of glutaraldehyde.

In another instance of large-scale use, the side leather tanner is producing a mellow, drum-dyed, full-grain, waxed or lightly finished leather for work shoes, hunters' boots and casual shoes. Casual shoes are unlined and benefit from greater perspiration resistance. A number of colors are more intense so that it has been possible to reduce the amount of dye. The composition of the fat liquor was not changed, but the amount was reduced. Staking has been improved in that the desired mellowness is obtained without looseness. In other words, the leather is relatively tight and has a good break in spite of being mellow.

To cite quite a different approach, one side leather tanner is using a glutaraldehyde retannage on his "softy" leather primarily because the feel of the grain is improved. It produces a "silky" feel which eliminated the rather harsh, "dry" feel that he was trying to overcome.

At least two side leather tanners are using glutaraldehyde on their white leather to improve the perspiration resistance of nurses' shoes. The amount of glutaraldehyde is kept to

the minimum necessary to produce a significant improvement in the leather because the color is changed from a blue-white to a cream white. The amount is as low as 3% of the commercial 25% solution and is not over 5%. The regular pigment finish helps to mask the cream shade.

Another and more recent application on side leather is the addition of glutaraldehyde to the regular tannage for insole leather. The chrome-tanned sides are retanned with glutaraldehyde and an extract blend. The glutaraldehyde is added first, the sides are drummed and vegetable extract is then added to the same liquor. The amount of fat liquor was reduced. Insole leather provides a desirable outlet for hides with considerable grain imperfections. Insole leather of 8-9 oz. for men's shoes is produced.

Glutaraldehyde has been used for several years for retanning cut insoles in a dipping procedure. These are usually vegetable-tanned insoles, which is outside of my subject.

So far, side leather has been emphasized almost to the exclusion of other leathers. It is correct that most of the glutaraldehyde used for tanning is used by the side leather branch of the industry. Calf and kid dress shoes are not usually subjected to severe conditions. The chrome tannage, itself, provides adequate perspiration resistance. This would be even more true of European chrome-tanned leather which usually contains more chrome than United States leathers. Glutaraldehyde is used as a retannage on some calf leather which is to be used in the manufacture of unlined

shoes. I do not know of any application on kid leather. Goatskin lining leather would appear to be the logical place to evaluate a glutaraldehyde retannage.

There are a number of applications that are interesting but which might be called specialty items. Glutaraldehyde is being used as a retannage of chrome-tanned kangaroo skins to increase the perspiration resistance for boot upper leather. The first commercial use of glutaraldehyde was on Turkish sheepskins. These sheepskins in particular have a firm backbone and neck. The use of glutaraldehyde softened these areas without making the garment leather loose. The leather was upgraded, and glutaraldehyde was quickly adopted.

A development that has produced an attractive as well as a more useful product is the application of glutaraldehyde to the tanning of woolskins or shearlings. Shearlings have been used for many years in a limited way for the prevention and cure of decubitus ulcers, commonly known as bedsores. There is no doubt of their efficacy, but their limitation was poor washability. Glutaraldehyde used as a pre-tan, a simultaneous tan, or a retan improves the washability so markedly that shearlings are now practical for use as medical pads. The same shearlings are recapturing the paint roller market which was lost to synthetic fibers. This is due to the greater resistance to alkaline solutions and to chemicals in general as compared to conventional tannages. The golden color of the wool is due entirely to the reaction of glutaraldehyde with the keratin.

A recent development on sheepskins is the use of glutaraldehyde to increase the perspiration resistance of fine glove leather. This is a successful British development by BLMRA and English tanners in the production of leather for aviators' gloves. It is interesting not only because of its importance but also because this application accentuates all of the limitations of this tannage. It has succeeded in spite of the disadvantages because these have been minimized by using the right amount of glutaraldehyde and the most desirable procedure to obtain a careful balance of properties. Again, a retannage of the regular chrome-tanned leather is most practical. I assume that the minimum amount of glutaraldehyde has been used to produce a worthwhile increase in perspiration resistance while minimizing the reduction in strength, the increased wettability and the increased tightness or loss of "run." I understand that some increase in the thickness of the leather has been permitted to compensate for the reduction in strength.

Summary

A number of compounds used to retan chrome-tanned leather and the properties they confer to the leather have been described. The initiative of the industry in applying new chemicals and processes to "tailor-make" leather for specific end-uses is noteworthy. These, together with the advances made in mechanization and automation, thoroughly refute the all-too-common idea that the leather industry is backward.